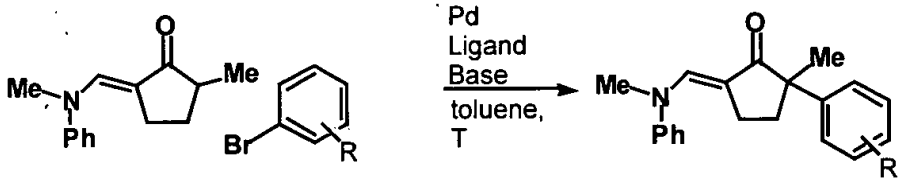
**Figure 1**

Examples of the Asymmetric Arylation of 2-Methylcyclopentanone Bearing a Blocking Group at the 5-Position

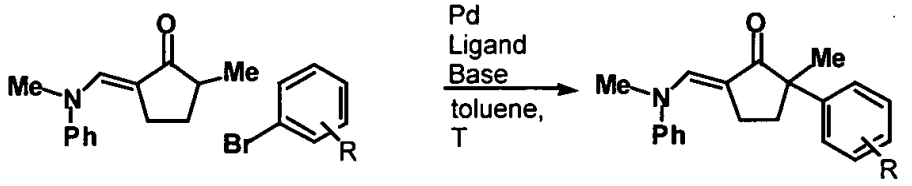



| R | Ligand | %Pd | %L | Base | T C° | Y% | ee % |
|---|---|---|---|---|---|---|---|
| 4-$^t$Bu | (S)-BINAP | 10 | 15 | NaHMDS | 100 | 67 | 90 |
| 4-$^t$Bu | (S)-BINAP | 10 | 15 | NaO$^t$Bu | 100 | 70 | 89 |
| 4-$^t$Bu | (R)-QUINAP | 5 | 7.5 | NaO$^t$Bu | 90 | 67 | 23 |
| 4-$^t$Bu | (R)-MOP | 10 | 15 | KO$^t$Bu | 100 | 68 | 34 |
| 4-$^t$Bu | (S)-BINAP | 10 | 15 | KO$^t$Bu | 100 | 54 | 84 |
| 4-$^t$Bu | (R)-QUINAP | 10 | 15 | KO$^t$Bu | 100 | 23 | 15 |
| 4-$^t$Bu | (S)-BINAP | 10 | 15 | KO$^t$Bu | 100 | 63 | 85 |
| 4-$^t$Bu | (S)-BINAP | 10 | 15 | KHMDS | 100 | 51 | 86 |
| 4-$^t$Bu | (-)-**1** | 5 | 7.5 | NaO$^t$Bu | rt | 93 | 68 |
| 4-$^t$Bu | (-)-**1** | 5 | 7.5 | NaO$^t$Bu | rt | 99 | 67 |
| 3-OMe | (S)-BINAP | 10 | 15 | NaO$^t$Bu | 100 | 91 | 85 |
| 4-OMe | (S)-BINAP | 5 | 10 | NaO$^t$Bu | 100 | 55 | 62 |
| 4-OMe | (S)-BINAP | 10 | 15 | NaO$^t$Bu | 100 | 65 | 57 |
| 3-(2-dioxolane) | (S)-BINAP | 10 | 15 | NaO$^t$Bu | 100 | 96 | 86 |

[**1** = 2-(dicyclohexylphosphino)-2'-(dimethylamino)-1,1'-binaphthyl]

**Figure 2**

Additional Examples of the Asymmetric Arylation of 2-Methylcyclopentanone Bearing a Blocking Group at the 5-Position

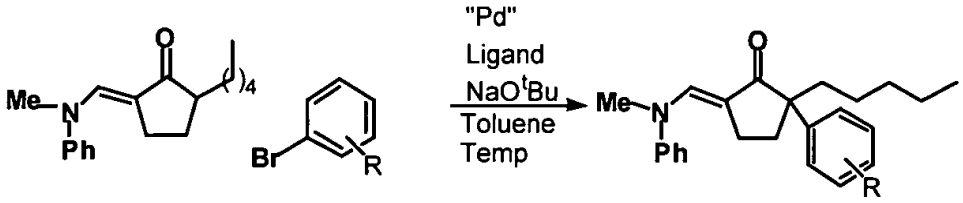



| R | Ligand | %Pd | %L | Base | T C° | Y% | ee % |
|---|---|---|---|---|---|---|---|
| 4-Me | (S)-BINAP | 10 | 15 | NaO$^t$Bu | 100 | 65 | 63 |
| 4-Me | (R)-QUINAP | 10 | 15 | NaO$^t$Bu | 100 | 82 | 25 |
| 4-Me | (-)-**1** | 5 | 7.5 | NaO$^t$Bu | rt | 88 | 75 |
| 2-Me | (S)-BINAP | 5 | 10 | NaO$^t$Bu | 100 | 52 | 10 |
| 2-Me | (S)-BINAP | 5 | 10 | NaO$^t$Bu | 100 | 48 | 8 |
| 3-Me | (S)-BINAP | 5 | 10 | NaO$^t$Bu | 100 | 70 | 80 |
| 3-Me | (S)-BINAP | 5 | 10 | NaO$^t$Bu | 100 | 72 | 80 |
| 4-$CF_3$ | (S)-BINAP | 10 | 15 | NaO$^t$Bu | 100 | 93 | 53 |
| 4-$CF_3$ | (S)-BINAP | 10 | 15 | NaO$^t$Bu | 80 | 80 | 44 |
| 4-$CF_3$ | (R)-QUINAP | 5 | 7.5 | NaO$^t$Bu | 90 | 54 | 43 |
| 3-$CF_3$ | (S)-BINAP | 5 | 7.5 | NaO$^t$Bu | 100 | 60 | 75 |
| 4-CN | (-)-**1** | 5 | 7.5 | NaO$^t$Bu | rt | 51 | 80 |

[**1** = 2-(dicyclohexylphosphino)-2'-(dimethylamino)-1,1'-binaphthyl]

**Figure 3**

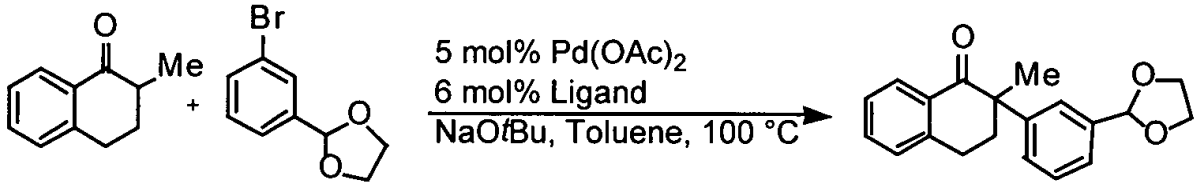
Asymmetric Arylation of 2-pentylcyclopentanone Bearing a Blocking Group at the 5-Position




| R | "Pd | Ligand | %Pd | %L | T C° | Y% | ee % |
|---|---|---|---|---|---|---|---|
| H | $Pd_2(dba)_3$ | (S)-BINAP | 10 | 15 | 93 | 84 | 93 |
| H | $Pd(OAc)_2$ | (-)-**1** | 10 | 15 | 72 | 78 | 72 |
| 3-Me | $Pd(OAc)_2$ | (S)-BINAP | 10 | 15 | 100 | 70 | 99 |
| 4-$CF_3$ | $Pd_2(dba)_3$ | (S)-BINAP | 10 | 15 | 100 | 71 | 90 |

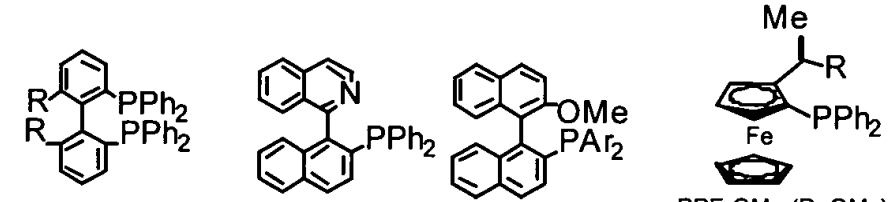
[**1** = 2-(dicyclohexylphosphino)-2'-(dimethylamino)-1,1'-binaphthyl]

**Figure 4** *α-Arylation of 2-Methyl-1-Tetralone--Ligand Effects*

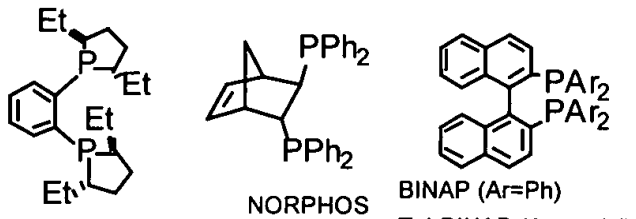



| Ligand | Yield | ee |
|---|---|---|
| (S)-BINAP | 69 | 84 |
| (R)-QUINAP | 43 | 84 |
| (R)-MeO-BIPHEP | 59 | 85 |
| (S)-BIPHEMP | 39 | 82 |
| (R,R)-NORPHOS | 38 | 40 |
| (R)-MOP | 19 | 8 |
| (R)-PPF-OMe | 38 | 1 |
| (R)-(S)-JOSIPHOS | 38 | 2 |
| (S)-Et-DUPHOS [a] | 8 | 12 |
| (S)-Tol-BINAP [b] | 26 | 30 |

(a) Reaction run with 10 mol% $Pd_2(dba)_3$, 24 mol% (S)-Tol-BINAP, NaHMDS as base. (b) Reaction run with 2.5 mol% $Pd_2(dba)_3$, 6 mol% (S)-Et-DUPHOS, NaHMDS as base.

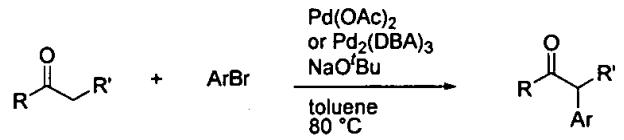


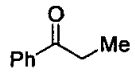
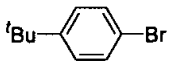
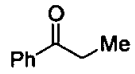
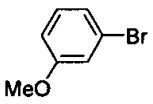
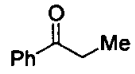
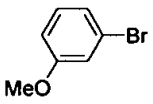
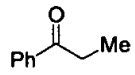
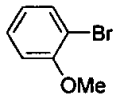
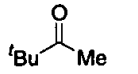
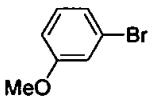
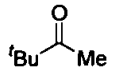
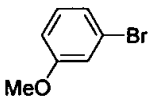
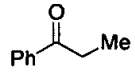
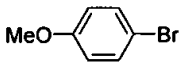
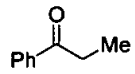
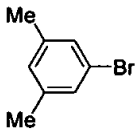
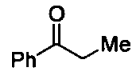
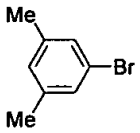
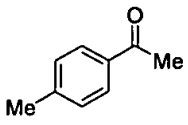
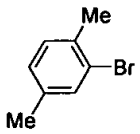

BIPHEMP (R=Me)
MeO-BIPHEP (R=OMe)
QUINAP
MOP
PPF-OMe (R=OMe)
JOSIPHOS (R=PCy2)




Et-DUPHOS
NORPHOS
BINAP (Ar=Ph)
Tol-BINAP (Ar=p-tolyl)

**Figur 5.** α-Arylations of Ketones in the Absence of a Phosphine Ligand.




| entry | Ketone | Aryl Bromide | Pd Source (mol %) | (% yield) |
|---|---|---|---|---|
| 1 |  |  | $Pd_2(DBA)_3$ (1.5 mol %) | 55% |
| 2 |  |  | $Pd_2(DBA)_3$ (1.5 mol %) | 54% |
| 3 |  |  | $Pd(OAc)_2$ (1 mol %) | 79% |
| 4 |  |  | $Pd_2(DBA)_3$ (1.5 mol %) | 46% |
| 5 |  |  | $Pd_2(DBA)_3$ (1.5 mol %) | 48% |
| 6 |  |  | $Pd(OAc)_2$ (1 mol %) | 71% |
| 7 |  |  | $Pd(OAc)_2$ (1 mol %) | 79% |
| 8 |  |  | $Pd(OAc)_2$ (1 mol %) | 83% |
| 9 |  |  | $Pd_2(DBA)_3$ (0.5 mol %) | 79% |
| 10 |  |  | $Pd(OAc)_2$ (1.0 mol %) | 64% |